**PCT** WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C11D 3/395, 3/16 — A1

(11) International Publication Number: WO 00/60045

(43) International Publication Date: 12 October 2000 (12.10.00)

(21) International Application Number: PCT/US00/08690

(22) International Filing Date: 30 March 2000 (30.03.00)

(30) Priority Data:
60/127,426 1 April 1999 (01.04.99) US

(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: PERKINS, Christopher, Mark [US/US]; 7230 Fernbank Avenue, Cincinnati, OH 45233 (US).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217–1087 (US).

(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published**

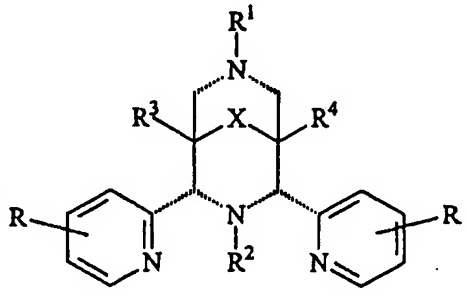
*With international search report.*

*Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: TRANSITION METAL BLEACHING AGENTS

(57) Abstract

The present invention relates to a bleaching system comprising: a) from about 1ppb, by weight of a transition metal catalyst comprising: i) a transition metal; ii) a ligand having formula (I): wherein each R is independently hydrogen, hydroxyl, $C_1$–$C_4$ alkyl, and mixtures thereof; $R^1$ is $C_1$–$C_4$ alkyl, $C_6$–$C_{10}$ aryl, and mixtures thereof; $R^2$ is $C_1$–$C_4$ alkyl, $C_6$–$C_{10}$ aryl, and mixtures thereof; $R^3$ and $R^4$ are each independently hydrogen, $C_1$–$C_8$ alkyl, $C_1$–$C_8$ hydroxyalkyl, $-(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$–$C_4$alkyl, x is from 0 to 4, and mixtures thereof; X is carbonyl, $-C(R^6)_2-$ wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$–$C_4$ alkyl, and mixtures thereof; b) optionally a source of hydrogen peroxide; and c) the balance carriers and adjunct ingredients.



(I)

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | | | TR | Turkey |
| BG | Bulgaria | HU | Hungary | ML | Mali | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MN | Mongolia | UA | Ukraine |
| BR | Brazil | IL | Israel | MR | Mauritania | UG | Uganda |
| BY | Belarus | IS | Iceland | MW | Malawi | US | United States of America |
| CA | Canada | IT | Italy | MX | Mexico | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NE | Niger | VN | Viet Nam |
| CG | Congo | KE | Kenya | NL | Netherlands | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NO | Norway | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | NZ | New Zealand | | |
| CM | Cameroon | | | PL | Poland | | |
| CN | China | KR | Republic of Korea | PT | Portugal | | |
| CU | Cuba | KZ | Kazakstan | RO | Romania | | |
| CZ | Czech Republic | LC | Saint Lucia | RU | Russian Federation | | |
| DE | Germany | LI | Liechtenstein | SD | Sudan | | |
| DK | Denmark | LK | Sri Lanka | SE | Sweden | | |
| EE | Estonia | LR | Liberia | SG | Singapore | | |

# TRANSITION METAL BLEACHING AGENTS

## FIELD OF THE INVENTION

The present invention relates to bleaching and detergent compositions which comprise a catalytically effective amount of a transition-metal bleach catalyst which is a complex of a transition-metal and an ultrarigid bicyclic ligand. The present invention further relates to a method for bleaching/cleaning fabric with a catalytically effective amount of said transition-metal bleach catalyst wherein the method is performed substantially free of any organic or inorganic peroxygen compound or precursors to any organic or inorganic peroxygen compound.

## BACKGROUND OF THE INVENTION

Bleaching of fabric is essentially exposing soiled or stained fabric to a chemical reaction the purpose of which is to eliminate the soil or stain. At one point in time, bleaching involved exposure of fabric to a solution of hypochlorite. Therefore, fabric which was colored or dyed via sensitive pigments were excluded from treatment with bleach. To the benefit of the consumer, formulators developed various forms of bleach *inter alia* peroxygen bleaching systems which typically comprise a source of hydrogen peroxide and a bleach activator. This combination of source of hydrogen peroxide and activator plays a dominating role in effective, safe bleaching compositions. An effective example of this peroxygen bleaching system employs perborate (peroxygen source) and nonanoyloxybenzene sulfonate (activator).

One of the most effective bleaching systems is the transition metal complex wherein a transition metal and a suitable ligand are chemically combined to form a bleaching catalyst. The goal of these bleaching catalysts is to produce catalysts which may be effective against certain types of stains *inter alia* carotenoid stains.

However, there still remains a need in the art for a bleaching system which will effectively bleach fabric without the need for reactive chemicals such as peroxides, sources of peroxide, and/or mixtures thereof.

## SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in that it has been surprisingly discovered that certain 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonanes are suitable for use as an ultrarigid bicyclic ligands which when combined with various transition metals, preferably, manganese(II), form transition metal complexes which serve as effective bleach catalysts. The bleach catalysts of the present invention can serve to accomplish the bleaching of soils and stains

in the absence of a source of hydrogen peroxide or other peroxygen bleaching agent. Alternatively, the transition metal complex bleaching agents of the present invention can be used to bleach peroxygen bleaching systems.

A first aspect of the present invention relates to bleaching compositions comprising:

a) a catalytically effective amount of a transition-metal bleach catalyst which is a complex of a transition-metal and a 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligand; and

b) the balance carriers and other adjunct ingredients;

provided said composition is substantially free of any organic or inorganic peroxygen compounds.

A further aspect of the present invention relates to compositions which comprise a peroxygen bleaching system, said composition comprising:

a) a catalytically effective amount of a transition-metal bleach catalyst which is a complex of a transition-metal and a 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligand;

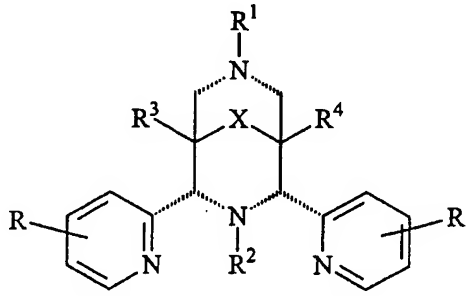
b) from about 1% by weight, of a peroxygen bleaching system comprising:

i) from about 40% to about 100% by weight, of the bleaching system, a source of hydrogen peroxide;

ii) optionally from about 0.1% to about 60% by weight, of the beaching system, a beach activator; and

c) the balance carriers and other adjunct ingredients.

The present invention also relates to transition-metal bleach catalysts which comprise a manganese (II) and/or a manganese (III) transition metal and an ultrarigid bicyclic ligand having the formula:



wherein each R is independently hydrogen, hydroxyl, halogen, $C_1$-$C_4$ alkyl, and mixtures thereof; $R^1$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^2$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^3$ and $R^4$ are each independently hydrogen, $C_1$-$C_8$ alkyl, $C_1$-$C_8$ hydroxyalkyl, -

$(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$-$C_4$ alkyl, and mixtures thereof, provided both $R^5$ units are not methyl, x is from 0 to 4, and mixtures thereof; X is carbonyl, $-C(R^6)_2-$ wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof, provided $R^3$ and $R^4$ are not both $C_1$ hydroxyalkyl when $R^1$ and $R^2$ are both methyl.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (° C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the surprising discovery that bleaching of soils and stains can be accomplished by a transition-metal catalyst comprising a 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligand either in the absence of a peroxygen bleach or source of hydrogen peroxide or in the presence of a peroxygen bleaching system. Sources of peroxygen bleaches include, but are not limited to, sources of hydrogen peroxide *inter alia* hydrogen peroxide, percarbonate, perborate. Alkali metal and alkaline earth metal percarbonate and perborate are typically found in laundry bleaching systems. These sources of hydrogen peroxide are typically formulated with one or more bleach activators *inter alia* nonanoyloxybenzenesulfonate (NOBS), tetraacetylethylenediamine (TAED). Bleach activators are typically viewed as precursors to the less stable but more reactive peroxyacid bleaching agents. Peroxyacids are formed *in situ* when the bleach activator (peroxyacid precursor) reacts with hydrogen peroxide or hydroperoxide anion via a perhydrolysis reaction. In addition, the bleaching systems of the present invention may also comprise a pre-formed peroxygen bleach *inter alia* nonanolylamide peroxyadipic acid (NAPAA).

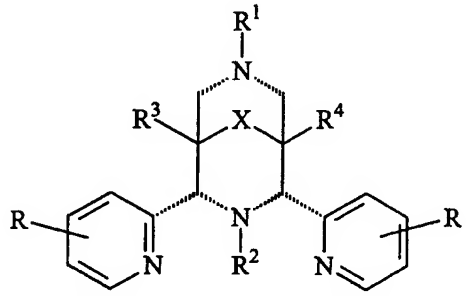
Transition metal bleaching component

i) Transition metal.

A first component of the transition metal bleaching component of the present invention is the transition metal which when taken together with the ultrarigid bicyclic ligands form the bleaching agent. Any transition metal which can complex with the hereinafter described 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligands to form an effect bleach catalyst are suitable for use in the present invention. A preferred transition metal is manganese (II), $Mn^{2+}$, which is capable of undergoing an oxidation/reduction cycle to manganese (III), $Mn^{3+}$.

ii) Ligands.

A second component of the transition metal bleaching component of the present invention is the 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligand having the general formula:



wherein each R is independently hydrogen, halogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof, preferably hydrogen, methyl, and mixtures thereof, more preferably hydrogen.

$R^1$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof, preferably methyl and benzyl.

$R^2$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof, preferably methyl and benzyl.

$R^3$ and $R^4$ are each independently hydrogen, $C_1$-$C_8$ alkyl, $C_1$-$C_8$ hydroxyalkyl, -$(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$-$C_4$ alkyl, and mixtures thereof, preferably methyl; x is from 0 to 4, preferably 0 or 1, more preferably 0.

X is carbonyl, -$C(R^6)_2$- wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof, preferably X is -$CH_2$- (methylene), -CHOH, -C(O)- (carbonyl), and mixtures thereof, more preferably -CHOH- and carbonyl.

Non-limiting examples of bleaching agents according to the present invention include:

dimethyl 3,7-dimethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate manganese(II) dichloride;

diethyl 3,7-dimethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate manganese(II) dichloride;

dimethyl 3,7-dimethyl-9-oxo-2,4-bis[2-(4-methyl)pyridyl]-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate manganese(II) dichloride;

dimethyl 3,7-diethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate manganese(II) dichloride;

dimethyl 3,7-dibenzyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate manganese(II) dichloride;

1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonan-9-ol manganese(II) dichloride;

1,5-bis(hydroxymethylene)-3,7-dibenzyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonan-9-ol manganese(II) dichloride;

1,5-bis(2-hydroxyethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonan-9-ol manganese(II) dichloride.

Bleaching Systems

The present invention relates to transition metal complexes and their use as bleaching agents in laundry and automatic dishwashing compositions. One aspect of the present invention relates to nil peroxygen bleach compositions comprising:

a) a catalytically effective amount of a transition-metal bleach catalyst which is a complex of a transition-metal and a 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligand; and

b) the balance carriers and other adjunct ingredients;

provided said composition is substantially free of any organic or inorganic peroxygen compounds.

Another aspect of the present invention relates to compositions which comprise a peroxygen bleaching system, said composition comprising:

a) a catalytically effective amount of a transition-metal bleach catalyst which is a complex of a transition-metal and a 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligand;

b) from about 1%, preferably from about 5% to about 80%, preferably to about 50% by weight, of a peroxygen bleaching system comprising:

i) from about 40%, preferably from about 50%, more preferably from about 60% to about 100%, preferably to about 95%, more preferably to about 80% by weight, of the bleaching system, a source of hydrogen peroxide;

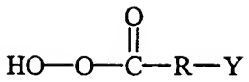
ii) optionally from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the beaching system, a beach activator; and

c) the balance carriers and other adjunct ingredients.

The bleaching systems of the present invention may also comprise one or more pre-formed bleaching agents, for example, composition which comprise:

a) a catalytically effective amount of a transition-metal bleach catalyst which is a complex of a transition-metal and a 2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane ligand;

b) from about 0.1%, preferably from about 0.5% to about 10%, preferably to about 5% by weight, of a pre-formed peroxygen bleach having the formula:



wherein R is a $C_1$-$C_{22}$ alkylene, $C_1$-$C_{22}$ substituted alkylene, phenylene, $C_6$-$C_{22}$ substituted phenylene, and mixtures thereof, Y is hydrogen, halogen, alkyl, aryl, -C(O)OH, -C(O)OOH, and mixtures thereof; and

c) the balance carriers and other adjunct ingredients.

Peroxygen Bleaching systems

The peroxygen bleaching systems of the present invention comprise a source of hydrogen peroxide and optionally, but preferably, a bleach activator. The following are non-limiting examples of peroxy bleaching system components which are suitable for use in the compositions of the present invention.

Hydrogen peroxide source

Sources of hydrogen peroxide which are suitable for use in the compositions of the present invention include, but are not limited to, perborates, percarbonates, perphosphates, persulfates, and mixtures thereof. Preferred sources of hydrogen peroxide are sodium perborate monohydrate, sodium perborate tetrahydrate, sodium percarbonate and sodium persulfate, more preferably are sodium perborate monohydrate, sodium perborate tetrahydrate, and sodium percarbonate. When present the source of hydrogen peroxide is present at a level of from about 40%, preferably from about 50%, more preferably from about 60% to about 100%, preferably to about 95%, more preferably to about 80% by weight, of the bleaching system. Embodiments which are bleach comprising pre-soak compositions may comprise from 5% to 99% of the source of hydrogen peroxide.

Bleach Activators

Preferably, the source of hydrogen peroxide (peroxygen bleach component) in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01%, preferably from about 0.5%, more preferably from about 1% to about 15%, preferably to about 10%, more preferably to about 8%, by weight of the composition. Also, bleach activators will comprise from about 0.1% to about 60% by weight, of the beaching system. When the herein described bleaching system comprises 60% by weight, of an activator (the maximal amount) and said composition (bleaching composition, laundry detergent, or otherwise) comprises 15% by weight of said activator (the maximal amount by weight), said composition will comprise 25% by weight of a bleaching system (60% of which is bleach activator, 40% a source of hydrogen peroxide). However, this is not meant to restrict the formulator to a 60:40 ratio of activator to hydrogen peroxide source.

Preferably the mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1, more preferably from about 10:1 to about 1:1, preferably to about 3:1.

Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate ($C_{10}$-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate ($C_8$-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred hydrophobic bleach activators include, but are not limited to, nonanoyloxybenzenesulphonate (NOBS), 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) an example of which is described in U.S. Patent No. 5,523,434, dodecanoyloxybenzenesulphonate (LOBS or $C_{12}$-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or $C_{11}$-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

Preferred bleach activators are those described in U.S. 5,698,504 Christie et al., issued December 16, 1997; U.S. 5,695,679 Christie et al. issued December 9, 1997; U.S. 5,686,401 Willey et al., issued November 11, 1997; U.S. 5,686,014 Hartshorn et al., issued November 11, 1997; U.S. 5,405,412 Willey et al., issued April 11, 1995; U.S. 5,405,413 Willey et al., issued April 11, 1995; U.S. 5,130,045 Mitchel et al., issued July 14, 1992; and U.S. 4,412,934 Chung et al., issued November 1, 1983, and copending patent applications U. S. Serial Nos. 08/709,072, 08/064,564; acyl lactam activators, as described in U.S. 5,698,504, U.S. 5,695,679 and U.S. 5,686,014, each of which is cited herein above, are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams, U.S. 5,503,639 Willey et al., issued April 2, 1996 all of which are incorporated herein by reference.

Quaternary substituted bleach activators may also be included. The present cleaning compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. 5,686,015 Willey et al., issued November 11, 1997; U.S. 5,654,421 Taylor et al., issued August 5, 1997; U.S. 5,460,747 Gosselink et al., issued October 24, 1995; U.S. 5,584,888 Miracle et al., issued December 17, 1996; and U.S. 5,578,136 Taylor et al., issued November 26, 1996; all of which are incorporated herein by reference.

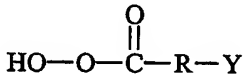
Highly preferred bleach activators useful herein are amide-substituted as described in U.S. 5,698,504, U.S. 5,695,679, and U.S. 5,686,014 each of which are cited herein above. Preferred examples of such bleach activators include: (6-octanamidocaproyl) oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate and mixtures thereof.

Other useful activators, disclosed in U.S. 5,698,504, U.S. 5,695,679, U.S. 5,686,014 each of which is cited herein above and U.S. 4,966,723Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a $C_6H_4$ ring to which is fused in the 1,2-positions a moiety --C(O)OC($R^1$)=N-.

Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

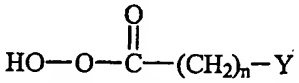
Pre-formed Bleaching Agents

The bleaching systems of the present invention may further comprise one or more pre-formed bleaching agents. Pre-formed bleaching materials typically have the general formula:



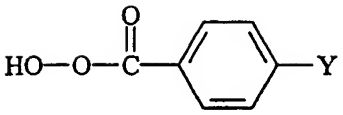
wherein R is a $C_1$-$C_{22}$ alkylene, $C_1$-$C_{22}$ substituted alkylene, phenylene, $C_6$-$C_{22}$ substituted phenylene, and mixtures thereof, Y is hydrogen, halogen, alkyl, aryl, -C(O)OH, -C(O)OOH, and mixtures thereof.

The organic percarboxylic acids usable in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic percarboxylic acid is aliphatic, the unsubstituted acid has the general formula:



wherein Y can be hydrogen, methyl, methyl chloride, carboxylate, percarboxylate; and n is an integer having the value from 1 to 20.

When the organic percarboxylic acid is aromatic, the unsubstituted acid has the general formula:



wherein Y can be hydrogen, alkyl, haloalkyl, carboxylate, percarboxylate, and mixtures thereof.

Typical monoperoxy percarboxylic acids useful herein include alkyl percarboxylic acids and aryl percarboxylic acids such as:

i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy-o-naphthoic acid;

ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxylauric acid, peroxystearic acid, and N,N-phthaloylaminoperoxycaproic acid (PAP).

Typical diperoxy percarboxylic acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as:

iii) 1,12-diperoxydodecanedioic acid;

iv) 1,9-diperoxyazelaic acid;

v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

vi) 2-decyldiperoxybutane-1,4-dioic acid;

vii) 4,4'-sulfonybisperoxybenzoic acid.

A non-limiting example of a highly preferred pre-formed bleach includes 6-nonylamino-6-oxoperoxycaproic acid (NAPAA) as described in U.S. Pat. No. 4,634,551 Burns et al., issued Jan. 6, 1987 included herein by reference.

## ADJUNCT INGREDIENTS

The bleaching, pre-soak, pre-treatment, laundry or automatic diswashing, or hard surface cleaning compositions of the present invention, whether granular, solid (bar), gel, or liquid may further comprise one or more carriers and adjunct ingredients.

Compositions according to the present invention may comprise:

a) a catalytically effective amount of a transition-metal bleach catalyst which is a complex of a transition-metal and an ultrarigid bicyclic ligand; and

b) optionally from about 0.001% to about 90% by weight, of one or more dye fixing agents;

c) optionally from about 0.01% to about 50% by weight, of one or more cellulose reactive dye fixing agents;

d) optionally from about 0.01% to about 15% by weight, of a chlorine scavenger;

e) optionally about 0.005% to about 1% by weight, of one or more crystal growth inhibitors;

f) optionally from about 0.01% to about 20% by weight, of a fabric abrasion reducing polymer;

g) optionally from about 1% to about 12% by weight, of one or more liquid carriers;

h) optionally from about 0.001% to about 1% by weight, of an enzyme;

i) optionally from about 0.01% to about 8% by weight, of a polyolefin emulsion or suspension;

j) optionally from about 0.01% to about 0.2% by weight, of a stabilizer;

k) optionally from about 1% to about 80% by weight, of a fabric softening active;

l) optionally less than about 15% by weight, of a principal solvent; and

m) from about 0.01%, preferably from about 0.1%, to about 60%, preferably to about 30% by weight, one or more surfactants, said surfactants selected from the group consisting of anionic, cationic, nonionic, ampholytic, zwitterionic surfactants, and mixtures thereof.

Surfactants

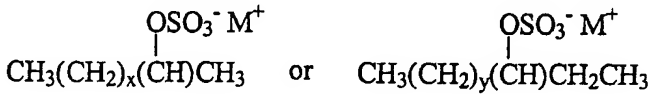
The bleaching, pre-soak, pre-treatment, and laundry detergent compositions of the present invention may comprise at least about 0.01% by weight, preferably from about 0.1% to about 60%, preferably to about 30% by weight, of a detersive surfactant system, said system is comprised of one or more category of surfactants depending upon the embodiment, said categories of surfactants are selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof. Within each category of surfactant, more than one type of surfactant of surfactant can be selected. For example, preferably the solid (i.e. granular) and viscous semi-solid (i.e. gelatinous, pastes, etc.) systems of the present invention, surfactant is preferably present to the extent of from about 0.1% to 60 %, preferably to about 30% by weight of the composition.

Nonlimiting examples of surfactants useful herein include:

a) $C_{11}$-$C_{18}$ alkyl benzene sulfonates (LAS);

b) $C_{10}$-$C_{20}$ primary, branched-chain and random alkyl sulfates (AS);

c) $C_{10}$-$C_{18}$ secondary (2,3) alkyl sulfates having the formula:



wherein x and (y + 1) are integers of at least about 7, preferably at least about 9; said surfactants disclosed in U.S. 3,234,258 Morris, issued February 8, 1966; U.S. 5,075,041

Lutz, issued December 24, 1991; U.S. 5,349,101 Lutz et al., issued September 20, 1994; and U.S. 5,389,277 Prieto, issued February 14, 1995 each incorporated herein by reference;

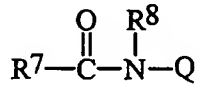
d) $C_{10}$-$C_{18}$ alkyl alkoxy sulfates ($AE_xS$) wherein preferably x is from 1-7;

e) $C_{10}$-$C_{18}$ alkyl alkoxy carboxylates preferably comprising 1-5 ethoxy units;

f) $C_{12}$-$C_{18}$ alkyl ethoxylates, $C_6$-$C_{12}$ alkyl phenol alkoxylates wherein the alkoxylate units are a mixture of ethyleneoxy and propyleneoxy units, $C_{12}$-$C_{18}$ alcohol and $C_6$-$C_{12}$ alkyl phenol condensates with ethylene oxide/propylene oxide block polymers *inter alia* Pluronic® ex BASF which are disclosed in U.S. 3,929,678 Laughlin et al., issued December 30, 1975, incorporated herein by reference;

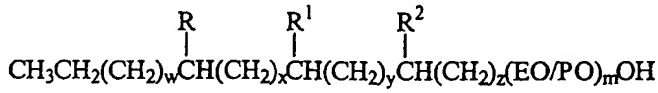
g) Alkylpolysaccharides as disclosed in U.S. 4,565,647 Llenado, issued January 26, 1986, incorporated herein by reference;

h) Polyhydroxy fatty acid amides having the formula:

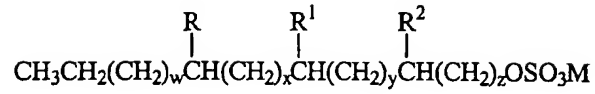


wherein $R^7$ is $C_5$-$C_{31}$ alkyl; $R^8$ is selected from the group consisting of hydrogen, $C_1$-$C_4$ alkyl, $C_1$-$C_4$ hydroxyalkyl, Q is a polyhydroxyalkyl moiety having a linear alkyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof; preferred alkoxy is ethoxy or propoxy, and mixtures thereof; preferred Q is derived from a reducing sugar in a reductive amination reaction, more preferably Q is a glycityl moiety; Q is more preferably selected from the group consisting of $-CH_2(CHOH)_nCH_2OH$, $-CH(CH_2OH)(CHOH)_{n-1}CH_2OH$, $-CH_2(CHOH)_2-(CHOR')(CHOH)CH_2OH$, and alkoxylated derivatives thereof, wherein n is an integer from 3 to 5, inclusive, and R' is hydrogen or a cyclic or aliphatic monosaccharide, which are described in U.S. 5,489,393 Connor et al., issued February 6, 1996; and U.S. 5,45,982 Murch et al., issued October 3, 1995, both incorporated herein by reference.

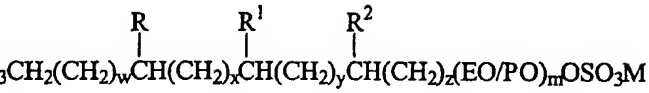
The bleaching, pre-soak, pre-treatment, and laundry detergent compositions of the present invention can also comprise from about 0.001% to about 100% of one or more (preferably a mixture of two or more) mid-chain branched surfactants, preferably mid-chain branched alkyl alkoxy alcohols having the formula:



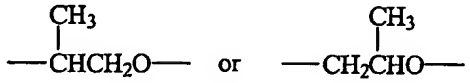
mid-chain branched alkyl sulfates having the formula:



and mid-chain branched alkyl alkoxy sulfates having the formula:



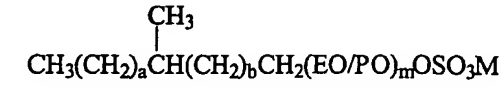
wherein the total number of carbon atoms in the branched primary alkyl moiety of these formulae (including the R, $R^1$, and $R^2$ branching, but not including the carbon atoms which comprise any EO/PO alkoxy moiety) is from 14 to 20, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 14.5 to about 17.5 (preferably from about 15 to about 17); R, $R^1$, and $R^2$ are each independently selected from hydrogen, $C_1$-$C_3$ alkyl, and mixtures thereof, preferably methyl; provided R, $R^1$, and $R^2$ are not all hydrogen and, when z is 1, at least R or $R^1$ is not hydrogen. M is a water soluble cation and may comprises more than one type of cation, for example, a mixture of sodium and potassium. The index w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; provided w + x + y + z is from 8 to 14. EO and PO represent ethyleneoxy units and propyleneoxy units having the formula:



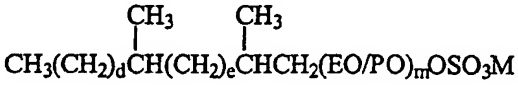
respectively, however, other alkoxy units *inter alia* 1,3-propyleneoxy, butoxy, and mixtures thereof are suitable as alkoxy units appended to the mid-chain branched alkyl moieties.

The mid-chain branched surfactants are preferably mixtures which comprise a surfactant system. Therefore, when the surfactant system comprises an alkoxylated surfactant, the index m indicates the average degree of alkoxylation within the mixture of surfactants. As such, the index m is at least about 0.01, preferably within the range of from about 0.1, more preferably from about 0.5, most preferably from about 1 to about 30, preferably to about 10, more preferably to about 5. When considering a mid-chain branched surfactant system which comprises only alkoxylated surfactants, the value of the index m represents a distribution of the average degree of alkoxylation corresponding to m, or it may be a single specific chain with alkoxylation (e.g., ethoxylation and/or propoxylation) of exactly the number of units corresponding to m.

The preferred mid-chain branched surfactants of the present invention which are suitable for use in the surfactant systems of the present invention have the formula:



or the formula:

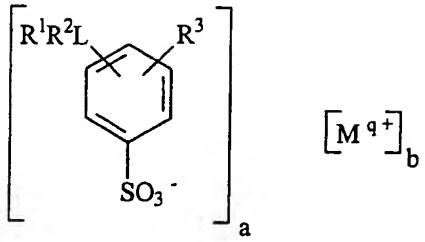


wherein a, b, d, and e are integers such that a + b is from 10 to 16 and d + e is from 8 to 14; M is selected from sodium, potassium, magnesium, ammonium and substituted ammonium, and mixtures thereof.

The surfactant systems of the present invention which comprise mid-chain branched surfactants are preferably formulated in two embodiments. A first preferred embodiment comprises mid-chain branched surfactants which are formed from a feedstock which comprises 25% or less of mid-chain branched alkyl units. Therefore, prior to admixture with any other conventional surfactants, the mid-chain branched surfactant component will comprise 25% or less of surfactant molecules which are non-linear surfactants.

A second preferred embodiment comprises mid-chain branched surfactants which are formed from a feedstock which comprises from about 25% to about 70% of mid-chain branched alkyl units. Therefore, prior to admixture with any other conventional surfactants, the mid-chain branched surfactant component will comprise from about 25% to about 70% surfactant molecules which are non-linear surfactants.

The surfactant systems of the laundry detergent compositions of the present invention can also comprise from about 0.001%, preferably from about 1%, more preferably from about 5%, most preferably from about 10% to about 100%, preferably to about 60%, more preferably to about 30% by weight, of the surfactant system, of one or more (preferably a mixture of two or more) mid-chain branched alkyl arylsulfonate surfactants, preferably surfactants wherein the aryl unit is a benzene ring having the formula:



wherein L is an acyclic hydrocarbyl moiety comprising from 6 to 18 carbon atoms; $R^1$, $R^2$, and $R^3$ are each independently hydrogen or $C_1$-$C_3$ alkyl, provided $R^1$ and $R^2$ are not attached at the terminus of the L unit; M is a water soluble cation having charge q wherein a and b are taken together to satisfy charge neutrality.

Builders

The compositions of the present invention, especially when comprising surfactants, preferably comprise one or more detergent builders or builder systems. When present, the compositions will typically comprise at least about 1% builder, preferably from about 5%, more preferably from about 10% to about 80%, preferably to about 50%, more preferably to about 30% by weight, of detergent builder.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates described in U.S. 4,664,839 Rieck, issued May 12, 1987. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6").

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Examples of suitable aluminosilicate builders are described in U.S. 4,274,975 Corkhill et al. included herein by reference. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$[M_z(zAlO_2)_y]\cdot xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Suitable are disclosed in U.S. 3,128,287 Berg, issued April 7, 1964, U.S. 3,635,830 Lamberti et al., issued January 18, 1972, U.S. 4,663,071 Bush et al., issued May 5, 1987, U.S. 3,923,679 Rapko, issued December 2, 1975; U.S. 4,158,635 Crutchfield et al., issued June 19, 1979; U.S. 4,120,874 Crutchfield et al., issued October 17, 1978; U.S. 4,566,984, Bush, issued January 28, 1986, U.S. 4,144,226, Crutchfield et al., issued March 13, 1979 and in U.S. 3,308,067, Diehl, issued March 7, 1967, Diehl U.S. Patent 3,723,322, and U.S. 4,102,903 Crutchfield et al., issued July 25, 1978 and further U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Dispersants

A description of other suitable polyalkyleneimine dispersants which may be optionally combined with the bleach stable dispersants of the present invention can be found in U.S. 4,597,898 Vander Meer, issued July 1, 1986; European Patent Application 111,965 Oh and Gosselink, published June 27, 1984; European Patent Application 111,984 Gosselink, published June 27, 1984; European Patent Application 112,592 Gosselink, published July 4, 1984; U.S.

4,548,744 Connor, issued October 22, 1985; and U.S. 5,565,145 Watson et al., issued October 15, 1996; all of which are included herein by reference. However, any suitable clay/soil dispersant or anti-redepostion agent can be used in the laundry compositions of the present invention.

In addition, polymeric dispersing agents which include polymeric polycarboxylates and polyethylene glycols, are suitable for use in the present invention. Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000, preferably from about 5,000, more preferably from about 7,000 to 100,000, more preferably to 75,000, most preferably to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Soil Release Agents

The compositions according to the present invention may optionally comprise one or more soil release agents. If utilized, soil release agents will generally comprise from about 0.01%, preferably from about 0.1%, more preferably from about 0.2% to about 10%, preferably to about 5%, more preferably to about 3% by weight, of the composition. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of the laundry cycle and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occuring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 5,728,671 Rohrbaugh *et al.*, issued March 17, 1998; U.S. 5,691,298 Gosselink *et al.*, issued November 25, 1997; U.S. 5,599,782 Pan *et al.*, issued February 4, 1997; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; U.S. 5,182,043 Morrall *et al.*, issued January 26, 1993; U.S. 4,956,447 Gosselink *et al.*, issued September 11, 1990; U.S. 4,976,879 Maldonado *et al.* issued December 11, 1990; U.S. 4,968,451 Scheibel *et al.*, issued November 6, 1990; U.S. 4,925,577 Borcher, Sr. *et al.*, issued May 15, 1990; U.S. 4,861,512 Gosselink, issued August 29, 1989; U.S. 4,877,896 Maldonado *et al.*, issued October 31, 1989; U.S. 4,771,730 Gosselink *et al.*, issued October 27, 1987; U.S. 711,730 Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580 Gosselink issued January 26, 1988; U.S. 4,000,093 Nicol *et al.*, issued December 28, 1976; U.S. 3,959,230 Hayes, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; and European Patent Application 0 219 048, published April 22, 1987 by Kud *et al.*

Further suitable soil release agents are described in U.S. 4,201,824 Voilland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681 Ruppert *et al.*; U.S. 4,220,918; U.S. 4,787,989; EP 279,134 A, 1988 to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N.V., 1974; all incorporated herein by reference.

Enzymes

"Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a liquid laundry, hard surface cleaning or personal care detergent composition. Preferred detersive enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for liquid laundry purposes include, but are not limited to, *inter alia* proteases, cellulases, lipases and peroxidases.

Protease Enzymes

The preferred liquid laundry detergent compositions according to the present invention further comprise at least 0.001% by weight, of a protease enzyme. However, an effective amount of protease enzyme is sufficient for use in the liquid laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. The protease enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Preferred liquid laundry detergent compositions of the present invention comprise modified protease enzymes derived from *Bacillus amyloliquefaciens* or *Bacillus lentus*. For the purposes of the present invention, protease enzymes derived from *B. amyloliquefaciens* are further referred to as "subtilisin BPN'" also referred to as "Protease A" and protease enzymes derived from *B. Lentus* are further referred to as "subtilisin 309". For the purposes of the present invention, the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al, entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, serves as the amino acid sequence numbering system for both subtilisin BPN' and subtilisin 309.

Derivatives of *Bacillus amyloliquefaciens* subtilisin -BPN' enzymes

A preferred protease enzyme for use in the present invention is a variant of Protease A (BPN') which is a non-naturally occurring carbonyl hydrolase variant having a different proteolytic activity, stability, substrate specificity, pH profile and/or performance characteristic as compared to the precursor carbonyl hydrolase from which the amino acid sequence of the variant is derived. This variant of BPN' is disclosed in EP 130,756 A, January 9, 1985. Specifically Protease A-BSV is BPN' wherein the Gly at position 166 is replaced with Asn, Ser, Lys, Arg, His,

Gln, Ala, or Glu; the Gly at position 169 is replaced with Ser; the Met at position 222 is replaced with Gln, Phe, Cys, His, Asn, Glu, Ala or Thr; or alternatively the Gly at position 166 is replaced with Lys, and the Met at position 222 is replaced with Cys; or alternatively the Gly at position 169 is replaced with Ala and the Met at position 222 is replaced with Ala.

Protease B

A preferred protease enzyme for use in the present invention is Protease B. Protease B is a non-naturally occurring carbonyl hydrolase variant having a different proteolytic activity, stability, substrate specificity, pH profile and/or performance characteristic as compared to the precursor carbonyl hydrolase from which the amino acid sequence of the variant is derived. Protease B is a variant of BPN' in which tyrosine is replaced with leucine at position +217 and as further disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985.

Bleach Stable Variants of Protease B (Protease B-BSV)

A preferred protease enzyme for use in the present invention are bleach stable variants of Protease B. Specifically Protease B-BSV are variants wherein the Gly at position 166 is replaced with Asn, Ser, Lys, Arg, His, Gln, Ala, or Glu; the Gly at position 169 is replaced with Ser; the Met at position 222 is replaced with Gln, Phe, Cys, His, Asn, Glu, Ala or Thr; or alternatively the Gly at position 166 is replaced with Lys, and the Met at position 222 is replaced with Cys; or alternatively the Gly at position 169 is replaced with Ala and the Met at position 222 is replaced with Ala.

Surface Active Variants of Protease B

Preferred Surface Active Variants of Protease B comprise BPN' wild-type amino acid sequence in which tyrosine is replaced with leucine at position +217, wherein the wild-type amino acid sequence at one or more of positions 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 218, 219 or 220 is substituted; wherein the BPN' variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin BPN'. Preferably, the positions having a substituted amino acid are 199, 200, 201, 202, 205, 207, 208, 209, 210, 211, 212, or 215; more preferably, 200, 201, 202, 205 or 207.

Also preferred proteases derived from *Bacillus amyloliquefaciens* subtilisin are subtilisin BPN' enzymes that have been modified by mutating the various nucleotide sequences that code for the enzyme, thereby modifying the amino acid sequence of the enzyme. These modified subtilisin enzymes have decreased adsorption to and increased hydrolysis of an insoluble substrate as compared to the wild-type subtilisin. Also suitable are mutant genes encoding for such BPN' variants.

Derivatives of subtilisin 309

Further preferred protease enzymes for use according to the present invention also include the "subtilisin 309" variants. These protease enzymes include several classes of subtilisin 309 variants described herein below.

Protease C

A preferred protease enzyme for use in the compositions of the present invention Protease C. Protease C is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

Protease D

A preferred protease enzyme for use in the present invention is Protease D. Protease D is a carbonyl hydrolase variant derived from *Bacillus lentus* subtilisin having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

A. Loop Region 6 Substitution Variants - These subtilisin 309-type variants have a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more of positions 193, 194, 195, 196, 197, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213 or 214; whereby the subtilisin 309 variant has decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309. Preferably these proteases have amino acids substituted at 193, 194, 195, 196, 199, 201, 202, 203, 204, 205, 206 or 209; more preferably 194, 195, 196, 199 or 200.

B. Multi-Loop Regions Substitution Variants - These subtilisin 309 variants may also be a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence, wherein the modified amino acid sequence comprises a substitution at one or more positions in one or more of the first, second, third, fourth, or fifth loop regions; whereby the subtilisin 309 variant has

decreased adsorption to, and increased hydrolysis of, an insoluble substrate as compared to the wild-type subtilisin 309.

C. Substitutions at positions other than the loop regions - In addition, one or more substitution of wild-type subtilisin 309 may be made at positions other than positions in the loop regions, for example, at position 74. If the additional substitution to the subtilisin 309 is mad at position 74 alone, the substitution is preferably with Asn, Asp, Glu, Gly, His, Lys, Phe or Pro, preferably His or Asp. However modifications can be made to one or more loop positions as well as position 74, for example residues 97, 99, 101, 102, 105 and 121.

Subtilisin BPN' variants and subtilisin 309 variants are further described in WO 95/29979, WO 95/30010 and WO 95/30011, all of which were published November 9, 1995, all of which are incorporated herein by reference.

A further preferred protease enzyme for use in combination with the modified polyamines of the present invention is ALCALASE® from Novo. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble . When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Other particularly useful proteases are multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128; 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262,

263, 265, 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT Application Nos. PCT/US98/22588, PCT/US98/22482 and PCT/US98/22486 all filed on October 23, 1998 from The Procter & Gamble Company (P&G Cases 7280&, 7281& and 7282L, respectively). More preferably the protease variant includes a substitution set selected from the group consisting of:

12/76/103/104/130/222/245/261;
62/103/104/159/232/236/245/248/252;
62/103/104/159/213/232/236/245/248/252;
62/101/103/104/159/212/213/232/236/245/248/252;
68/103/104/159/232/236/245;
68/103/104/159/230/232/236/245;
68/103/104/159/209/232/236/245;
68/103/104/159/232/236/245/257;
68/76/103/104/159/213/232/236/245/260;
68/103/104/159/213/232/236/245/248/252;
68/103/104/159/183/232/236/245/248/252;
68/103/104/159/185/232/236/245/248/252;
68/103/104/159/185/210/232/236/245/248/252;
68/103/104/159/210/232/236/245/248/252;
68/103/104/159/213/232/236/245;
98/103/104/159/232/236/245/248/252;
98/102/103/104/159/212/232/236/245/248/252;
101/103/104/159/232/236/245/248/252;
102/103/104/159/232/236/245/248/252;
103/104/159/230/236/245;
103/104/159/232/236/245/248/252;

103/104/159/217/232/236/245/248/252;
103/104/130/159/232/236/245/248/252;
103/104/131/159/232/236/245/248/252;
103/104/159/213/232/236/245/248/252; and
103/104/159/232/236/245.

Still even more preferably the protease variant includes a substitution set selected from the group consisting of:

12R/76D/103A/104T/130T/222S/245R/261D;
62D/103A/104I/159D/232V/236H/245R/248D/252K;
62D/103A/104I/159D/213R/232V/236H/245R/248D/252K;
68A/103A/104I/159D/209W/232V/236H/245R;
68A/76D/103A/104I/159D/213R/232V/236H/245R/260A;
68A/103A/104I/159D/213E/232V/236H/245R/248D/252K;
68A/103A/104I/159D/183D/232V/236H/245R/248D/252K;
68A/103A/104I/159D/232V/236H/245R;
68A/103A/104I/159D/230V/232V/236H/245R;
68A/103A/104I/159D/232V/236H/245R/257V;
68A/103A/104I/159D/213G/232V/236H/245R/248D/252K;
68A/103A/104I/159D/185D/232V/236H/245R/248D/252K;
68A/103A/104I/159D/185D/210L/232V/236H/245R/248D/252K;
68A/103A/104I/159D/210L/232V/236H/245R/248D/252K;
68A/103A/104I/159D/213G/232V/236H/245R;
98L/103A/104I/159D/232V/236H/245R/248D/252K;
98L/102A/103A/104I/159D/212G/232V/236H/245R/248D/252K;
101G/103A/104I/159D/232V/236H/245R/248D/252K;
102A/103A/104I/159D/232V/236H/245R/248D/252K;
103A/104I/159D/230V/236H/245R;
103A/104I/159D/232V/236H/245R/248D/252K;
103A/104I/159D/217E/232V/236H/245R/248D/252K;
103A/104I/130G/159D/232V/236H/245R/248D/252K;
103A/104I/131V/159D/232V/236H/245R/248D/252K;
103A/104I/159D/213R/232V/236H/245R/248D/252K; and

103A/104I/159D/232V/236H/245R.

Most preferably the protease variant includes the substitution set 101/103/104/159/232/236/245/248/252, preferably 101G/103A/104I/159D/232V/236H/245R/248D/252K.

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Commercially available proteases useful in the present invention are known as ESPERASE®, ALCALASE®, DURAZYM®, SAVINASE®, EVERLASE® and KANNASE® all from Novo Nordisk A/S of Denmark, and as MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® all from Genencor International (formerly Gist-Brocades of The Netherlands).

In addition to the above-described protease enzymes, other enzymes suitable for use in the liquid laundry detergent compositions of the present invention are further described herein below.

Other Enzymes

Enzymes in addition to the protease enzyme can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable enzymes include amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for

current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from about 0.001%, preferably from about 0.01% to about 5%, preferably to about 1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents, it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Amylases suitable herein include, for example, α-amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide / tetraacetylethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Baccillus* amylases, especially the *Bacillus* α-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position

variation of a similar parent amylase, such as *B. amyloliquefaciens, B. subtilis,* or *B. stearothermophilus;* (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants

stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139 McCarty et al., issued January 5, 1971. Enzymes are further disclosed in U.S. 4,101,457 Place et al, issued July 18, 1978, and U.S. 4,507,219 Hughes, issued March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868 Hora et al., issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319 Gedge et al., issued August 17, 1971; EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

A further preferred enzyme according to the present invention are mannanase enzymes. When present mannanase enzymes comprise from about 0.0001%, preferably from 0.0005%, more preferably from about 0.001% to about 2%, preferably to about 0.1% more preferably to about 0.02% by weight, of said composition.

Preferably, the following three mannans-degrading enzymes : EC 3.2.1.25 : β-mannosidase, EC 3.2.1.78 : Endo-1,4-β-mannosidase, referred therein after as "mannanase" and EC 3.2.1.100 : 1,4-β-mannobiosidase (IUPAC Classification- Enzyme nomenclature, 1992 ISBN 0-12-227165-3 Academic Press) are useful in the compositions of the present invention.

More preferably, the detergent compositions of the present invention comprise a β-1,4-Mannosidase (E.C. 3.2.1.78) referred to as Mannanase. The term "mannanase" or "galactomannanase" denotes a mannanase enzyme defined according to the art as officially being named mannan endo-1,4-beta-mannosidase and having the alternative names beta-mannanase and endo-1,4-mannanase and catalysing the reaction: random hydrolysis of 1,4-beta-D- mannosidic linkages in mannans, galactomannans, glucomannans, and galactoglucomannans.

In particular, Mannanases (EC 3.2.1.78) constitute a group of polysaccharases which degrade mannans and denote enzymes which are capable of cleaving polyose chains containing mannose units, i.e. are capable of cleaving glycosidic bonds in mannans, glucomannans, galactomannans and galactogluco-mannans. Mannans are polysaccharides having a backbone composed of β-1,4- linked mannose; glucomannans are polysaccharides having a backbone or more or less regularly alternating β-1,4 linked mannose and glucose; galactomannans and galactoglucomannans are mannans and glucomannans with α-1,6 linked galactose sidebranches. These compounds may be acetylated.

The degradation of galactomannans and galactoglucomannans is facilitated by full or partial removal of the galactose sidebranches. Further the degradation of the acetylated mannans, glucomannans, galactomannans and galactogluco-mannans is facilitated by full or partial deacetylation. Acetyl groups can be removed by alkali or by mannan acetylesterases. The oligomers which are released from the mannanases or by a combination of mannanases and α-galactosidase and/or mannan acetyl esterases can be further degraded to release free maltose by β-mannosidase and/or β-glucosidase.

Mannanases have been identified in several *Bacillus* organisms. For example, Talbot et al., *Appl. Environ. Microbiol.*, Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus* in dimer form having molecular weight of 162 kDa and an optimum pH of 5.5-7.5. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from *Bacillus subtilis* having a molecular weight of 38 kDa, an optimum activity at pH 5.0 and 55C and a pI of 4.8. JP-03047076 discloses a beta-mannanase derived from *Bacillus* sp., having a molecular weight of 373 kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. JP-63056289 describes the production of an alkaline, thermostable beta-mannanase which hydrolyses beta-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno-oligosaccharides. JP-63036774 relates to the *Bacillus* microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase at an alkaline pH. JP-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp. AM-001. A purified mannanase from *Bacillus amyloliquefaciens* useful in the bleaching of pulp and paper and a method of preparation thereof is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active at an extreme pH and temperature. WO 94/25576 discloses an enzyme from *Aspergillus aculeatus*, CBS 101.43, exhibiting mannanase activity which may be useful for degradation or modification of plant or algae cell wall material. WO 93/24622 discloses a mannanase isolated from *Trichoderma reseei* useful for bleaching lignocellulosic pulps. An hemicellulase capable of degrading mannan-

containing hemicellulose is described in WO91/18974 and a purified mannanase from *Bacillus amyloliquefaciens* is described in WO97/11164.

Preferably, the mannanase enzyme will be an alkaline mannanase as defined below, more preferably, a mannanase originating from a bacterial source. Especially, the laundry detergent composition of the present invention will comprise an alkaline mannanase selected from the mannanase from the strain *Bacillus agaradherens* NICMB 40482; the mannanase from *Bacillus* strain 168, gene yght; the mannanase from *Bacillus sp.* I633 and/or the mannanase from *Bacillus sp.* AAI12. Most preferred mannanase for the inclusion in the detergent compositions of the present invention is the mannanase enzyme originating from *Bacillus sp.* I633 as described in the co-pending application No. PA 1998 01340.

The terms "alkaline mannanase enzyme" is meant to encompass an enzyme having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a given pH ranging from 7 to 12, preferably 7.5 to 10.5.

The alkaline mannanase from *Bacillus agaradherens* NICMB 40482 is described in the co-pending U.S. patent application serial No. 09/111,256. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus agaradherens*, NCIMB 40482; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 32-343 of SEQ ID NO:2 as shown in U.S. patent application serial No. 09/111,256; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 97 to nucleotide 1029 as shown in U.S. patent application serial No. 09/111,256;

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 32 to amino acid residue 343 as shown in U.S. patent application serial No. 09/111,256;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pSJ1678 comprising the polynucleotide molecule (the DNA sequence) encoding said mannanase has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 18 May 1998 under the deposition number DSM 12180.

A second more preferred enzyme is the mannanase from the *Bacillus subtilis* strain 168, which is described in the co-pending U.S. patent application serial No. 09/095,163. More specifically, this mannanase is:

i) is encoded by the coding part of the DNA sequence shown in SED ID No. 5 shown in the U.S. patent application serial No. 09/095,163 or an analogue of said sequence; and/or

ii) a polypeptide comprising an amino acid sequence as shown SEQ ID NO:6 shown in the U.S. patent application serial No. 09/095,163; or

iii) an analogue of the polypeptide defined in ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed in the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO:5 as shown in the U.S. patent application serial No. 09/095,163

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO: 6 as shown in the U.S. patent application serial No. 09/095,163;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

A third more preferred mannanase is described in the co-pending Danish patent application No. PA 1998 01340. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* I633;

ii) a polypeptide comprising an amino acid sequence as shown in positions 33-340 of SEQ ID NO:2 as shown in the Danish application No. PA 1998 01340; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of:

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 317 to nucleotide 1243 the Danish application No. PA 1998 01340;

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 33 to amino acid residue 340 the Danish application No. PA 1998 01340;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM3 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 29 May 1998 under the deposition number DSM 12197.

A fourth more preferred mannanase is described in the Danish co-pending patent application No. PA 1998 01341. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* AAI 12;

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-362 of SEQ ID NO:2as shown in the Danish application No. PA 1998 01341; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of

a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 225 to nucleotide 1236 as shown in the Danish application No. PA 1998 01341;

b) species homologs of (a);

c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 25 to amino acid residue 362 as shown in the Danish application No. PA 1998 01341;

d) molecules complementary to (a), (b) or (c); and

e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM1 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 7 October 1998 under the deposition number DSM 12433.

The compositions of the present invention may also comprise a xyloglucanase enzyme. Suitable xyloglucanases for the purpose of the present invention are enzymes exhibiting endoglucanase activity specific for xyloglucan. The xyloglucanase is incorporated into the compositions of the invention preferably at a level of from 0.0001%, more preferably from 0.0005%, most preferably from 0.001% to 2%, preferably to 0.1%, more preferably to 0.02% by weight, of pure enzyme.

As used herein, the term "endoglucanase activity" means the capability of the enzyme to hydrolyze 1,4-β-D-glycosidic linkages present in any cellulosic material, such as cellulose, cellulose derivatives, lichenin, β-D-glucan, or xyloglucan. The endoglucanase activity may be determined in accordance with methods known in the art, examples of which are described in WO 94/14953 and hereinafter. One unit of endoglucanase activity (e.g. CMCU, AVIU, XGU or BGU) is defined as the production of 1 μmol reducing sugar/min from a glucan substrate, the glucan substrate being, e.g., CMC (CMCU), acid swollen Avicell (AVIU), xyloglucan (XGU) or cereal β-glucan (BGU). The reducing sugars are determined as described in WO 94/14953 and hereinafter. The specific activity of an endoglucanase towards a substrate is defined as units/mg of protein.

Suitable are enzymes exhibiting as its highest activity XGU endoglucanase activity (hereinafter "specific for xyloglucan"), which enzyme:

i) is encoded by a DNA sequence comprising or included in at least one of the following partial sequences:

a) ATTCATTTGT GGACAGTGGA C (SEQ ID No: 1)

b) GTTGATCGCA CATTGAACCA (SEQ ID NO: 2)

c) ACCCCAGCCG ACCGATTGTC (SEQ ID NO: 3)

d) CTTCCTTACC TCACCATCAT (SEQ ID NO: 4)

e) TTAACATCTT TTCACCATGA (SEQ ID NO: 5)

f) AGCTTTCCCT TCTCTCCCTT (SEQ ID NO: 6)

g) GCCACCCTGG CTTCCGCTGC CAGCCTCC (SEQ ID NO: 7)

h) GACAGTAGCA ATCCAGCATT (SEQ ID NO: 8)

i) AGCATCAGCC GCTTTGTACA (SEQ ID NO: 9)

j) CCATGAAGTT CACCGTATTG (SEQ ID NO: 10)

k) GCACTGCTTC TCTCCCAGGT (SEQ ID NO: 11)

l) GTGGGCGGCC CCTCAGGCAA (SEQ ID NO: 12)

m) ACGCTCCTCC AATTTTCTCT (SEQ ID NO: 13)

n) GGCTGGTAG TAATGAGTCT (SEQ ID NO: 14)

o) GGCGCAGAGT TTGGCCAGGC (SEQ ID NO: 15)

p) CAACATCCCC GGTGTTCTGG G (SEQ ID NO: 16)

q) AAAGATTCAT TTGTGGACAG TGGACGTTGA TCGCACATTG AACCAACCCC AGCCGACCGA TTGTCCTTCC TTACCTCACC ATCATTTAAC ATCTTTTCAC CATGAAGCTT TCCCTTCTCT CCCTTGCCAC CCTGGCTTCC GCTGCCAGCC TCCAGCGCCG CACACTTCTG CGGTCAGTGG GATACCGCCA CCGCCGGTGA CTTCACCCTG TACAACGACC TTTGGGGCGA GACGGCCGGC ACCGGCTCCC AGTGCACTGG AGTCGACTCC TACAGCGGCG ACACCATCGC TTGTCACACC AGCAGGTCCT GGTCGGAGTA GCAGCAGCGT CAAGAGCTAT GCCAACG (SEQ ID NO:17) or

r) CAGCATCTCC ATTGAGTAAT CACGTTGGTG TTCGGTGGCC CGCCGTGTTG CGTGGCGGAG GCTGCCGGGA GACGGGTGGG GATGGTGGTG GGAGAGAATG TAGGGCGCCG TGTTTCAGTC CCTAGGCAGG ATACCGGAAA ACCGTGTGGT AGGAGGTTTA TAGGTTTCCA GGAGACGCTG TATAGGGGAT AAATGAGATT GAATGGTGGC CACACTCAAA CCAACCAGGT CCTGTACATA

CAATGCATAT ACCAATTATA CCTACCAAAA AAAAAAAAAA AAAAAAAAAA AAAA (SEQ ID NO:18)

or a sequence homologous thereto encoding a polypeptide specific for xyloglucan with endoglucanase activity,

ii) is immunologically reactive with an antibody raised against a highly purified endoglucanase encoded by the DNA sequence defined in i) and derived from *Aspergillus aculeatus*, CBS 101.43, and is specific for xyloglucan.

More specifically, as used herein the term "specific for xyloglucan" means that the endoglucanase enzyme exhibits its highest endoglucanase activity on a xyloglucan substrate, and preferably less than 75% activity, more preferably less than 50% activity, most preferably less than about 25% activity, on other cellulose-containing substrates such as carboxymethyl cellulose, cellulose, or other glucans.

Preferably, the specificity of an endoglucanase towards xyloglucan is further defined as a relative activity determined as the release of reducing sugars at optimal conditions obtained by incubation of the enzyme with xyloglucan and the other substrate to be tested, respectively. For instance, the specificity may be defined as the xyloglucan to β-glucan activity (XGU/BGU), xyloglucan to carboxy methyl cellulose activity (XGU/CMCU), or xyloglucan to acid swollen Avicell activity (XGU/AVIU), which is preferably greater than about 50, such as 75, 90 or 100.

The term "derived from" as used herein refers not only to an endoglucanase produced by strain CBS 101.43, but also an endoglucanase encoded by a DNA sequence isolated from strain CBS 101.43 and produced in a host organism transformed with said DNA sequence. The term "homologue" as used herein indicates a polypeptide encoded by DNA which hybridizes to the same probe as the DNA coding for an endoglucanase enzyme specific for xyloglucan under certain specified conditions (such as presoaking in 5xSSC and pre-hybridizing for 1 h at -40°C in a solution of 5xSSC, 5xDenhardt's solution, and 50 μg of denatured sonicated calf thymus DNA, followed by hybridization in the same solution supplemented with 50 μCi 32-P-dCTP labeled probe for 18 h at -40°C and washing three times in 2xSSC, 0.2% SDS at 40°C for 30 minutes). More specifically, the term is intended to refer to a DNA sequence which is at least 70% homologous to any of the sequences shown above encoding an endoglucanase specific for xyloglucan, including at least 75%, at least 80%, at least 85%, at least 90% or even at least 95% with any of the sequences shown above. The term is intended to include modifications of any of the DNA sequences shown above, such as nucleotide substitutions which do not give rise to another amino acid sequence of the polypeptide encoded by the sequence, but which correspond to the codon usage of the host organism into which a DNA construct comprising any of the DNA sequences is introduced or nucleotide substitutions which do give rise to a different amino acid

sequence and therefore, possibly, a different amino acid sequence and therefore, possibly, a different protein structure which might give rise to an endoglucanase mutant with different properties than the native enzyme. Other examples of possible modifications are insertion of one or more nucleotides into the sequence, addition of one or more nucleotides at either end of the sequence, or deletion of one or more nucleotides at either end or within the sequence.

Endoglucanase specific for xyloglucan useful in the present invention preferably is one which has a XGU/BGU, XGU/CMU and/or XGU/AVIU ratio (as defined above) of more than 50, such as 75, 90 or 100.

Furthermore, the endoglucanase specific for xyloglucan is preferably substantially devoid of activity towards β-glucan and/or exhibits at the most 25% such as at the most 10% or about 5%, activity towards carboxymethyl cellulose and/or Avicell when the activity towards xyloglucan is 100%. In addition, endoglucanase specific for xyloglucan of the invention is preferably substantially devoid of transferase activity, an activity which has been observed for most endoglucanases specific for xyloglucan of plant origin.

Endoglucanase specific for xyloglucan may be obtained from the fungal species *A. aculeatus*, as described in WO 94/14953. Microbial endoglucanases specific for xyloglucan has also been described in WO 94/14953. Endoglucanases specific for xyloglucan from plants have been described, but these enzymes have transferase activity and therefore must be considered inferior to microbial endoglucanases specific for xyloglucan whenever extensive degradation of xyloglucan is desirable. An additional advantage of a microbial enzyme is that it, in general, may be produced in higher amounts in a microbial host, than enzymes of other origins.

Enzyme Stabilizing System

Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001%, preferably from about 0.005%, more preferably from about 0.01% to about 10%, preferably to about 8%, more preferably to about 6% by weight, of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type

of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species disclosed in U.S. 4,537,706 Severson, issued August 27, 1985. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions may further comprise from 0, preferably from about 0.01% to about 10%, preferably to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium

perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392 Baginski et al., issued March 24, 1987.

## METHOD OF USE

The present invention further relates to a method for bleaching fabric comprising the step of contacting fabric with an aqueous solution comprising at least 1 ppb of a transition metal catalyst or alternatively contacting the fabric with a laundry detergent comprising:

a) from about 1 ppb by weight of a transition metal catalyst according to the present invention;

b) from about 0.01% by weight, of a surfactant system; and

c) the balance carriers and other adjunct ingredients.

Preferably the aqueous solution comprises at least about 0.01%, preferably at least about 1% by weight, of said laundry detergent composition.

The following is a non-limiting example of the preparation of a bleach catalyst which effectively bleaches stains in the absence of a source of peroxygen.

## EXAMPLE 1

Preparation of dimethyl 3,7-dimethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo-[3.3.1]nonane-1,5-dicarboxylate manganese(II) dichloride. The ligand 3,7-dimethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo-[3.3.1]nonane-1,5-dicarboxylate, hereinafter "$L^1$", is prepared by published literature methods, *inter alia*, R. Haller, *Arch. Pharm.*, 1968, **301**, 741 and R. Haller, *Arch. Pharm.*, 1968, **302**, 113.

A solution of $MnCl_2 \cdot 4H_2O$ (67 mg, 0.34 mmol) in methanol (4 ml) is added to a hot solution of $L^1$ (150 mg, 0.34 mmol) in methanol (5 ml). This was refluxed for 15 minutes and stored overnight at 5° C. The yellow precipitate was filtered off, washed with cold ethanol,

recrystallised from ethanol/methanol and vacuum dried. Yield: approximately 0.16 g (0.28 mmol. ~ 84%).

EXAMPLE 2

Preparation of 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonan-9-ol manganese(II) dichloride. Sodium tetrahydroborate (6.47 g, 0.171 mol) is added slowly to a cooled suspension of $L^1$ (7.5 g, 17.10 mmol) (prepared as in Example 1 above) in 250 ml absolute methanol; the temperature is maintained below 0° C. After stirring at room temperature for 12 h the solvent is removed under reduced pressure. The solid product was dissolved in water (400 ml), and the solution is stirred for 2 h. The white suspension is extracted with chloroform (400 ml), the solvent removed and the solid is stirred in hydrochloric acid (10%, 200 ml) for I hr. The solution is neutralized with NaOH and extracted with chloroform (400 ml), and the organic phase is dried over magnesium sulfate. The solvent is then removed under reduced pressure to afford a white solid, wherein the yield is about 4.2 g of crude product.

The crude product is dissolved in absolute THF (150 ml) and added dropwise to a filtered solution of $LiAlH_4$ (1.55 g, 40.8 mmol) in absolute THF (41 ml). The solution is stirred for 12 h at room temperature and the resulting solution is treated with an aqueous solution of sodium tartrate. The resulting layers are separated and the aqueous phase extracted with chloroform (100 ml). The organic phases are combined and a like volume of chloroform is added. The organic phase is dried over magnesium sulfate and the solvent removed under reduced pressure. Recrystallization from methanol/ethanol affords 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonan-9-ol, hereinafter "$L^2$", in about 35% yield.

A solution of $MnCl_2 \cdot 4H_2O$ (0.618 g, 3.121 mmol) in methanol (10 ml) is added to a hot solution of $L^2$ (1.2 g, 3.121 mmol) in methanol (10 ml). This was refluxed for 15 minutes and the solvent is removed by rotary evaporation to yield an orange powder which is recrystallised from ethanol to yield about 1.2 g (76%) of 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonan-9-ol manganese(II) dichloride $1/2H_2O$.

The following are non-limiting examples of the bleaching system of the present invention.

TABLE I

weight %

| Ingredients | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| $C_{14}$-$C_{15}$ alkyl E1.0 sulfate | 22.5 | 22.5 | 22.5 | 22.5 |
| Linear alkyl benzene sulfonate | 3.0 | 3.0 | 3.0 | 3.0 |

| | | | | |
|---|---|---|---|---|
| $C_{10}$ amidopropyl DMA | 1.5 | 1.5 | 1.5 | 1.5 |
| $C_{12}$-$C_{14}$ alkyl E7.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Citric Acid | 2.5 | 2.5 | 2.5 | 2.5 |
| $C_{12}$-$C_{18}$ alkyl fatty acid | 3.5 | 3.5 | 3.5 | 3.5 |
| Rapeseed fatty acid | 5.0 | 5.0 | 5.0 | 5.0 |
| protease | 0.8 | 1.57 | 1.57 | 1.57 |
| amylase | 0.055 | 0.088 | 0.088 | 0.088 |
| cellulase | 0.188 | 0.055 | 0.055 | 0.055 |
| lipolase | 0.06 | -- | -- | -- |
| mannanase | 0.007 | 0.0033 | 0.0033 | 0.0033 |
| Sodium metaborate | 2.0 | 2.5 | 2.5 | 2.5 |
| Ca formate/$CaCl_2$ | 0.02 | 0.10 | 0.10 | 0.10 |
| Bleach catalyst [1] | 0.035 | 0.034 | 0.034 | 0.034 |
| Anti-oxidant [2] | 0.23 | 0.25 | 0.25 | 0.25 |
| Reducing agent [3] | 0.02 | -- | -- | -- |
| Reducing agent [4] | -- | -- | 0.0042 | 0.0083 |
| Hydrophobic dispersant [5] | 0.65 | 0.76 | 0.76 | 0.76 |
| Soil release agent [6] | 0.147 | -- | -- | -- |
| Soil release agent [7] | -- | 0.10 | 0.10 | 0.10 |
| Suds suppresser | 0.60 | 0.60 | 0.60 | 0.60 |
| Water and minors | balance | balance | balance | balance |

1. 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonan-9-ol manganese(II) dichloride 1/2$H_2O$.
2. Butylated hydroxy toluene.
3. Potassium metabisulfite.
4. Potassium sulfite.
5. PEI 189 E15-18 according to U.S. Patent 4,597,898 Vander Meer, issued July 1, 1986.
6. Soil release agent according to U.S. Patent 4,702,857 Gosselink, issued October 27, 1987.
7. Soil release agent according to U.S. Patent 4,968,451, Scheibel *et al.*, issued November 6, 1990.

The following examples include compositions which comprise an adjunct bleaching agent.

TABLE II

weight %

| Ingredients | 7 | 8 | 9 | 10 |
|---|---|---|---|---|
| Sodium $C_{11}$-$C_{13}$ alkylbenzene-sulfonate | 13.3 | 13.7 | 10.4 | 11.1 |
| Sodium $C_{14}$-$C_{15}$ alcohol sulfate | 3.9 | 4.0 | 4.5 | 11.2 |
| Sodium $C_{14}$-$C_{15}$ alcohol ethoxylate (0.5) sulfate | 2.0 | 2.0 | -- | -- |
| Sodium $C_{14}$-$C_{15}$ alcohol ethoxylate (6.5) | 0.5 | 0.5 | 0.5 | 1.0 |
| Tallow fatty acid | -- | -- | -- | 1.1 |
| Sodium tripolyphosphate | -- | 41.0 | -- | -- |
| Zeolite A, hydrate (0.1-10 micron size) | 26.3 | -- | 21.3 | 28.0 |
| Sodium carbonate | 23.9 | 12.4 | 25.2 | 16.1 |
| Sodium Polyacrylate (45%) | 3.4 | -- | 2.7 | 3.4 |
| Sodium silicate (1:6 ratio NaO/$SiO_2$)(46%) | 2.4 | 6.4 | 2.1 | 2.6 |
| Sodium sulfate | 10.5 | 10.9 | 8.2 | 15.0 |
| Sodium perborate | 1.0 | 1.0 | 5.0 | -- |
| Poly(ethyleneglycol), MW ~4000 (50%) | 1.7 | 0.4 | 1.0 | 1.1 |
| Citric acid | -- | -- | 3.0 | -- |
| Bleach catalyst [1] | 0.035 | 0.030 | 0.034 | 0.028 |
| Bleach activator [2] | -- | -- | 5.9 | -- |
| Soil release agent [3] | -- | 0.10 | 0.10 | 0.10 |
| Suds suppresser | 0.60 | 0.60 | 0.60 | 0.60 |
| Water and minors [4] | balance | balance | balance | balance |

1. 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonan-9-ol manganese(II) dichloride 1/2$H_2O$.
2. Nonyl ester of sodium p-hydroxybenzene-sulfonate.
3. Soil release agent according to U.S. 5,415,807 Gosselink et al., issued May 16, 1995.
4. Balance to 100% can, for example, include minors like optical brightener, perfume, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including $CaCO_3$, talc, silicates, etc.

The following is a non-limiting example of the bleaching system of the present invention in the absence of a source of hydrogen peroxide.

TABLE III

weight %

| Ingredients | 11 | 12 | 13 | 14 |
|---|---|---|---|---|
| Sodium $C_{11}$-$C_{13}$ alkylbenzene-sulfonate | 13.3 | 13.7 | 10.4 | 11.1 |
| Sodium $C_{14}$-$C_{15}$ alcohol sulfate | 3.9 | 4.0 | 4.5 | 11.2 |
| Sodium $C_{14}$-$C_{15}$ alcohol ethoxylate (0.5) sulfate | 2.0 | 2.0 | -- | -- |
| Sodium $C_{14}$-$C_{15}$ alcohol ethoxylate (6.5) | 0.5 | 0.5 | 0.5 | 1.0 |
| Tallow fatty acid | -- | -- | -- | 1.1 |
| Sodium tripolyphosphate | -- | 41.0 | -- | -- |
| Zeolite A, hydrate (0.1-10 micron size) | 26.3 | -- | 21.3 | 28.0 |
| Sodium carbonate | 23.9 | 12.4 | 25.2 | 16.1 |
| Sodium Polyacrylate (45%) | 3.4 | -- | 2.7 | 3.4 |
| Sodium silicate (1:6 ratio $NaO/SiO_2$)(46%) | 2.4 | 6.4 | 2.1 | 2.6 |
| Sodium sulfate | 10.5 | 10.9 | 8.2 | 15.0 |
| Poly(ethyleneglycol), MW ~4000 (50%) | 1.7 | 0.4 | 1.0 | 1.1 |
| Citric acid | -- | -- | 3.0 | -- |
| Bleach catalyst [1] | 0.10 | 0.07 | 0.035 | 0.028 |
| Anti-oxidant [2] | 0.23 | 0.25 | 0.25 | 0.25 |
| Reducing agent [3] | 0.02 | -- | -- | -- |
| Reducing agent [4] | -- | -- | 0.0042 | 0.0083 |
| Hydrophobic dispersant [5] | 0.65 | 0.76 | 0.76 | 0.76 |
| Soil release agent [6] | 0.147 | 0.10 | 0.10 | 0.10 |
| Suds suppresser | 0.60 | 0.60 | 0.60 | 0.60 |
| Water and minors [7] | balance | balance | balance | balance |

1. 1,5-bis(hydroxymethylene)-3,7-dimethyl-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonan-9-ol manganese(II) dichloride $1/2H_2O$.
2. Potassium metabisulfite.
3. Potassium sulfite.
4. PEI 189 E15-18 according to U.S. Patent 4,597,898 Vander Meer, issued July 1, 1986.
6. Soil release agent according to U.S. 5,415,807 Gosselink et al., issued May 16, 1995.
7. Balance to 100% can, for example, include minors like optical brightener, perfume, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including $CaCO_3$, talc, silicates, etc.

The compositions of the present invention can be suitably prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. 5,691,297

Nassano et al., issued November 11, 1997; U.S. 5,574,005 Welch et al., issued November 12, 1996; U.S. 5,569,645 Dinniwell et al., issued October 29, 1996; U.S. 5,565,422 Del Greco et al., issued October 15, 1996; U.S. 5,516,448 Capeci et al., issued May 14, 1996; U.S. 5,489,392 Capeci et al., issued February 6, 1996; U.S. 5,486,303 Capeci et al., issued January 23, 1996 all of which are incorporated herein by reference.

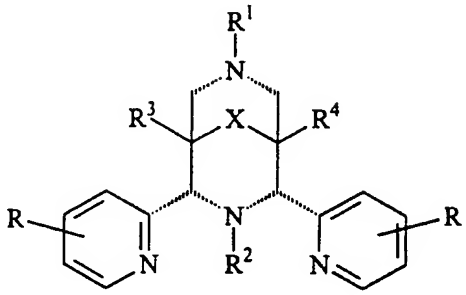
What is claimed is:

1. A bleaching system comprising:

a) from 1 ppb, by weight of a transition metal catalyst comprising:

i) a transition metal;

ii) a ligand having the formula:



wherein each R is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof; $R^1$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^2$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^3$ and $R^4$ are each independently hydrogen, $C_1$-$C_8$ alkyl, $C_1$-$C_8$ hydroxyalkyl, $-(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$-$C_4$ alkyl, x is from 0 to 4, and mixtures thereof; X is carbonyl, $-C(R^6)_2-$ wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof;

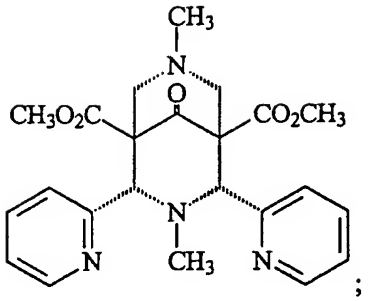
b) a source of hydrogen peroxide; and

c) the balance carriers and adjunct ingredients.

2. A composition according to Claim 1 wherein said transition metal is manganese(II).

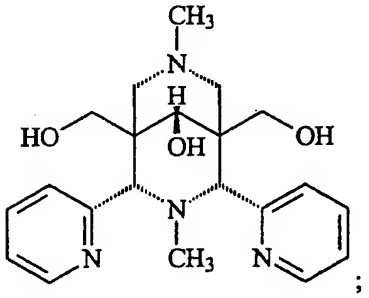
3. A composition according to either Claim 1 or 2 wherein said ligand has the formula selected from:

i)



;

ii)



;

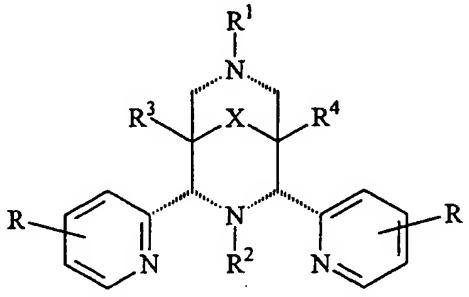
iii) and mixtures thereof.

4. A laundry detergent composition comprising:

a) from 1 ppb, by weight of a transition metal catalyst comprising:

i) a transition metal;

ii) a ligand having the formula:



wherein each R is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof; $R^1$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^2$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^3$ and $R^4$ are each independently hydrogen, $C_1$-$C_8$ alkyl, $C_1$-$C_8$ hydroxyalkyl, $-(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$-$C_4$ alkyl, x is from 0 to 4, and mixtures thereof; X is carbonyl, $-C(R^6)_2-$ wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof;

b) a source of hydrogen peroxide;

c) from 0.01% by weight, of a detersive surfactant selected from the group consisting of cationic, anionic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof; and

d) the balance carriers and adjunct ingredients.

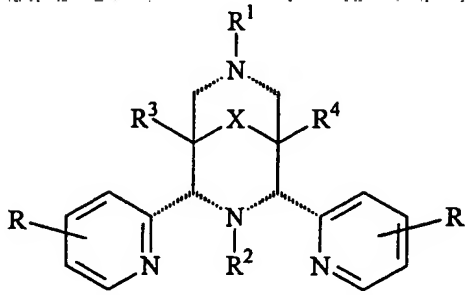
5. A composition according to Claim 4 wherein said adjunct ingredients are selected from the group consisting of builders, optical brighteners, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

6. A bleaching system comprising:

a) from 1 ppb, by weight of a transition metal catalyst comprising:

i) a transition metal;

ii) a ligand having the formula:



wherein each R is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof; $R^1$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^2$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^3$ and $R^4$ are each independently hydrogen, $C_1$-$C_8$ alkyl, $C_1$-$C_8$ hydroxyalkyl, $-(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$-$C_4$ alkyl, x is from 0 to 4, and mixtures thereof; X is carbonyl, $-C(R^6)_2-$ wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof; and

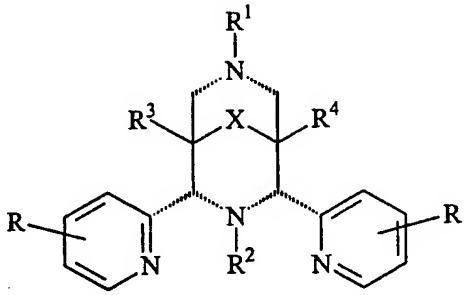
b) the balance carriers and adjunct ingredients.

7. A laundry detergent composition comprising:

a) from 1 ppb, by weight of a transition metal catalyst comprising:

i) a transition metal;

ii) a ligand having the formula:



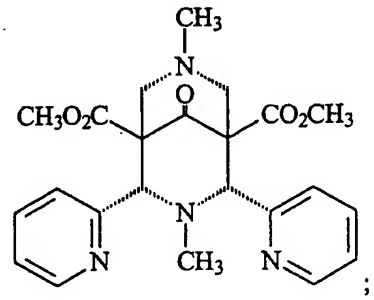
wherein each R is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof; $R^1$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^2$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^3$ and $R^4$ are each independently hydrogen, $C_1$-$C_8$ alkyl, $C_1$-$C_8$ hydroxyalkyl, $-(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$-$C_4$ alkyl, x is from 0 to 4, and mixtures thereof; X is carbonyl, $-C(R^6)_2-$ wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof;

b) from 0.01% by weight, of a detersive surfactant selected from the group consisting of cationic, anionic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof; and

c) the balance carriers and adjunct ingredients.

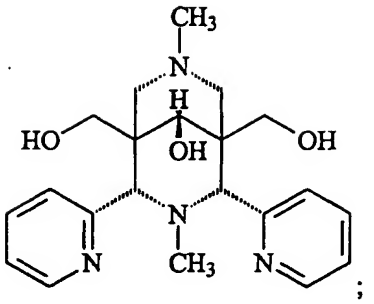
8. A composition according to any of Claims 4-7 comprising a transition metal catalyst wherein said transition metal is manganese(II) and said ligand has the formula selected from:

i)



;

ii)



;

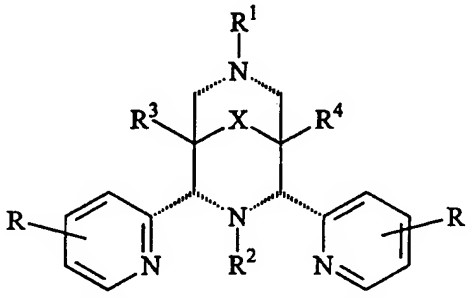
iii) and mixtures thereof.

9. A composition according to any of Claims 4-8 wherein said adjunct ingredients are selected from the group consisting of builders, optical brighteners, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.

10. A method for bleaching fabric comprising the step of contacting fabric with an aqueous solution comprising at least 1 ppb of a transition metal catalyst having the formula:

i) a transition metal;

ii) a ligand having the formula:



wherein each R is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof; $R^1$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^2$ is $C_1$-$C_4$ alkyl, $C_6$-$C_{10}$ aryl, and mixtures thereof; $R^3$ and $R^4$ are each independently hydrogen, $C_1$-$C_8$ alkyl, $C_1$-$C_8$ hydroxyalkyl, $-(CH_2)_xCO_2R^5$ wherein $R^5$ is $C_1$-$C_4$ alkyl, x is from 0 to 4, and mixtures thereof; X is carbonyl, $-C(R^6)_2-$ wherein each $R^6$ is independently hydrogen, hydroxyl, $C_1$-$C_4$ alkyl, and mixtures thereof.

# INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 00/08690

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/395 C11D3/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | EP 0 544 519 A (UNILEVER PLC ;UNILEVER NV (NL)) 2 June 1993 (1993-06-02) claims 1-11 | 1-10 |
| A | US 3 919 102 A (KUHLING DIETER ET AL) 11 November 1975 (1975-11-11) claims 1-15 | 1-10 |
| A | WO 98 39098 A (COLLINSON SIMON ROBERT ;BUSCH DARYLE HADLEY (US); HUBIN TIMOTHY JA) 11 September 1998 (1998-09-11) claims 1-19 | 1-10 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 31 July 2000 | 07/08/2000 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | RICHARDS, M |



Form PCT/ISA/210 (second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/US 00/08690

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0544519 A | 02-06-1993 | US 5194416 A | 16-03-1993 |
| | | AU 652867 B | 08-09-1994 |
| | | AU 2969292 A | 27-05-1993 |
| | | BR 9204548 A | 01-06-1993 |
| | | CA 2083658 A,C | 27-05-1993 |
| | | CN 1075163 A,B | 11-08-1993 |
| | | DE 69216786 D | 27-02-1997 |
| | | DE 69216786 T | 15-05-1997 |
| | | ES 2097291 T | 01-04-1997 |
| | | JP 6121933 A | 06-05-1994 |
| | | KR 9608938 B | 10-07-1996 |
| | | KR 9615159 B | 01-11-1996 |
| | | MX 9206810 A | 01-07-1993 |
| | | ZA 9209186 A | 26-05-1994 |
| US 3919102 A | 11-11-1975 | US 3825543 A | 23-07-1974 |
| | | DE 2112557 A | 21-09-1972 |
| | | FR 2130312 A | 03-11-1972 |
| | | GB 1379170 A | 02-01-1975 |
| | | IT 950070 B | 20-06-1973 |
| | | DE 2112678 A | 28-09-1972 |
| | | FR 2182781 A | 14-12-1973 |
| WO 9839098 A | 11-09-1998 | AU 6226498 A | 22-09-1998 |
| | | EP 0966323 A | 29-12-1999 |
| | | ZA 9801883 A | 01-09-1998 |